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13. ABSTRACT (Maximum 200 words)

Nanoscale materials, devices and systems are currently of wide interest in science and technology. We report a novel approach for preparing functional, electroactive and photoactive nanostructured polymeric materials which uses the inherent phase separation of rod - coil block copolymer systems. A series of novel polyester-polybenzobisthiazole-polyester triblock copolymers was designed, synthesized, and investigated to explore various issues of the self-assembly, solid-state electronic properties and optical properties of nanostructured polymeric materials. The self-assembly or phase separation process as well as the photophysical properties of the resulting nanophase-separated materials are shown to vary with the length of the coil-like block when the electroactive and photoactive rodlike block length is fixed. Because the rodlike blocks are electroactive and photoactive, optical techniques can be used as powerful probes of the self-assembly process and the resulting nanostructures.

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Electroactive and Photoactive Nanostructured Materials From Self-Assembling Coil-Rod-Coil Triblock Copolymers

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1. Introduction

Nanoscale materials, devices, and systems offer many opportunities and challenges for science and technology [1-4]. In the case of electroactive and photoactive materials, nanostructure can lead to novel phenomena and properties not observed in the bulk materials owing to quantum confinement and size effects [4]. The two fundamental approaches to creating such nanostructured materials, devices, and systems are through: (i) the reduction of bulk materials and components to sizes of order 100 nm or less by microlithography or related methods (i.e., the "top down" approach); and (ii) the assembly of molecules into supramolecular structures and systems of nanometer dimensions (i.e., the "bottom up" approach) [1-4]. Here, we offer a novel example of the latter approach to nanostructured materials. Specifically, we explore the self-assembly properties of rod-coil polymer systems as a means to the synthesis of electroactive and photoactive nanophase polymeric materials.

The driving force for self-assembly in rod-coil polymer systems arises from the *thermodynamic incompatibility* of the two vastly different conformations, the preference of the rodlike component for an *anisotropic phase*, and the attendant *phase separation* that occurs in mixtures of rodlike and coillike molecules [5,6]. Whereas such a phase separation or self-assembly of rod-coil polymer systems is the major technical barrier to achieving *single-phase molecular composites* of rod-coil polymers for structural applications, we view it as a novel approach to creating functional, electroactive, and photoactive *nanostructured polymer systems*. Nanophase-separated rod-coil polymer systems in which the rodlike component is electroactive and photoactive represent excellent model systems for investigating the effects of self-assembly, nanostructure, and composition on the electronic, optoelectronic, linear optical, and nonlinear optical properties of organic materials and polymers [6-12]. Our extensive prior studies of rod-coil polymer systems have included rod-coil polymer blends (molecular composites) [6,9] and random rod-coil copolymers [7,8,10]. Enhancement of third-order nonlinear optical (NLO) response was observed in the blends [9] and large enhancement of luminescence was observed in the rod-coil copolymers [7,8]. We have also achieved efficient electronic energy transfer in multichromophore polymer nanocomposite assemblies [10].

This paper reports the use of the self-assembly of $A_nB_mA_n$ coil-rod-coil triblock copolymer, where the block B_m is a conjugated rigid-rod polymer, to synthesize electroactive and photoactive nanophase-separated materials. Our approach is exemplified here by the synthesis and investigation of the series of polyester-polybenzobisthiazole-polyester triblock copolymers 1 shown in chart 1. The triblock contains a middle block of 2 which is rodlike, photoactive, and electroactive. The homopolymer 2, poly(p-phenylene benzobisthiazole) (PBZT), is a well-known conjugated rigid-rod polymer which has interesting photoconductive [11], light-emitting [7,8,12], and third-order nonlinear optical [9] properties. The coillike blocks of 1 consist of blocks of various lengths of the nonphotoactive and nonelectroactive polyester 3.

2. Experimental Section

The following procedure for 1a exemplifies the synthesis of the series of coil-rod-coil copolymers 1a-1e (Chart 1). The PBZT part of the triblock was synthesized first by the literature method which involves the

condensation of 2,5-diamino-1,4-benzenedithiol dihydrochloride (DABDT) and terephthalic acid (TA) in polyphosphoric acid (PPA) following the removal of hydrogen chloride [13]. In the synthesis of 1a, DABDT (0.441g, 1.8 mmol) was dissolved in 77% PPA (6.84g) in a glass reactor. After complete removal of hydrogen chloride from the reaction mixture of DABDT in PPA, TA (0.332g, 2 mmol) was added. P_2O_5 (3.1g) was then added to compensate for the theoretical water of condensation and provide 83% final P_2O_5 content in PPA. After stirring at 90°C for 3 hrs and 120°C for another 3 hrs to ensure sufficient time for removal of the last trace of HCl and wetting of the TA, the temperature was raised to 160°C and held for 24 hrs. The polymerization solution was cooled to 70°C and H_2O (1.6g) was added to adjust the PPA concentration to 72.45% (100% H_3PO_4). After stirring for 30 min, 1/10 portion of the eventual amount of total 16-hydroxyhexadecanoic acid (16-HA) (0.218g, 0.8 mmol) was added under positive pressure and the temperature was raised to 170°C. After 30 min, the temperature was lowered to 70°C again and another 1/10 portion of total 16-HA was added. The temperature of 170°C was reached and held for 4 hr. The addition of small portions of 16-HA several times helps to achieve a more narrow molecular weight distribution in the polyester part of the triblock. The red polymerization dope was precipitated into a large volume of water. The product was purified by refluxing in water for 2 days, followed by extraction with refluxing acetone in a soxhlet apparatus for 24 hrs. The reaction yields were typically 99-100%. After extraction with acetone for 24 hrs, the yields were still higher than 90%.

Copolymer solutions for 1H NMR spectroscopy were prepared in a dry box, using deuterated nitrobenzene ($C_6D_5NO_2$) containing aluminum (III) chloride. Solution processing of the polymers into films was achieved by using the method of reversible coordination complexation approach [6]. Thin films of good optical quality were prepared by casting in a dry box or by spin coating solution in nitrobenzene/ $AlCl_3$ onto silica substrates or casting from a mixed methanesulfonic acid (MSA)/dichloromethane (DCM) solvent followed by decomplexation in ethyl alcohol to obtain films of the pristine triblock copolymer. All photophysical measurements were done at room temperature and details will be reported elsewhere.

3. Results and Discussion

The polyester 3 (PHA) was synthesized by polyesterification of 16-HA in 72.45% PPA (100% H_3PO_4) medium at 170°C. 1H NMR, FTIR, DSC, and TGA characterization of the polyester confirmed its structure. The homopolymer PHA was semi-crystalline with a melting temperature of ~90°C and soluble in acetone from which good films could be cast or spin coated.

The series of triblock copolymers 1a-1e was synthesized by copolymerization of a carboxylic acid-terminated PBZT (2) with the AB-type monomer 16-HA in 72.45% PPA at 170°C. The resulting products of copolymerization were purified by extensive extraction with refluxing acetone which is a good solvent for the polyester. Many different experiments were done to establish the triblock copolymer nature of the materials, including 1H NMR, FTIR, UV-Vis, DSC, TGA, solubility, etc. The triblocks 1a-1e were not soluble in known solvents for either PBZT (e.g. MSA) or polyester (acetone, dichloromethane). However the triblocks were soluble in mixed MSA/dichloromethane (DCM) solvents or in nitrobenzene (NB)/ $AlCl_3$. DSC thermograms of the triblocks showed that all exhibited crystalline melting around 90°C and the enthalpy of fusion progressively increased from 1a to 1e in accord with the progressively increasing length of the polyester block. The 1H NMR spectra of 1a-1e in deuterated nitrobenzene containing $AlCl_3$ were obtained. The resonances and the number of protons corresponding to each resonance were in good agreement with the proposed structure. The compositions of the triblocks determined from 1H NMR spectra by the ratio of the 1,4-phenylene ring proton resonance to the aliphatic proton resonances were in good agreement with the feed compositions.

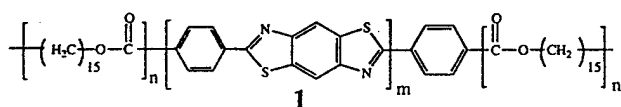
The expected phase separation or self-assembly process of coil-rod-coil triblock copolymers is illustrated in Figure 1. In isotropic solution, the triblock is in a disorder state. However, in the solid state the phase-separated ordered structure in which the rodlike blocks aggregate into an anisotropic domain is the thermodynamically stable structure [5,6]. Thus, the self-assembly process is a *kinetic process* that occurs during the coagulation of solutions into solids as well as during subsequent processing (e.g. annealing) of the solids. Because the rodlike blocks are electroactive and photoactive, optical techniques can be used as powerful probes of the self-assembly process and the resulting nanostructures. Figure 2 shows the optical absorption spectra of 1a, 1c, and 1d films cast from nitrobenzene/ AlCl_3 . The absorption bands of the triblocks have identical maxima at about 438 and 468 nm and a π - π^* absorption edge of 500 nm (2.48 eV). These triblocks with average of 9 repeat units of PBZT have essentially identical electronic absorption spectra as the high molecular weight homopolymer ($\overline{DP}_n \sim 150$) [7,8,11]. However, a novel feature of the UV-Vis spectra of the triblocks is the narrowing of the bandwidth of the main absorption band as the polyester block length increases (1a to 1c in Figure 2). A related trend was observed in the decay dynamics of the photoluminescence (PL) of the same films (inset of Figure 2). The origin of these effects is increasing chromophore confinement as the coil-like block length increases.

The steady-state PL spectra of 1c thin films prepared by three different methods are shown in Figure 3. In the inset of Figure 3 is the corresponding PL decay dynamics. The results reflect and evidence three degrees of chromophore aggregation during the self-assembly process of the same triblock.

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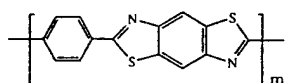
Chart 1



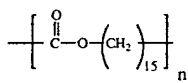
1a : m=9, n=2; 1d: m=9, n=9

1b: m=9, n=3; 1e: m=9, n=19

1c: m=9, n=4



2



3

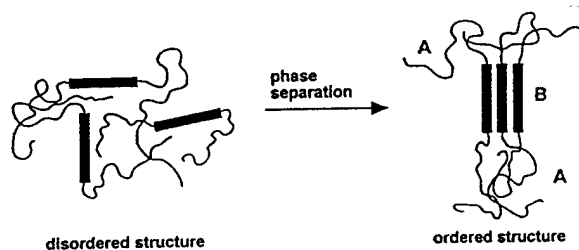


Figure 1. The self-assembly/phase separation of an ABA coil-rod-coil triblock copolymer used to synthesize nanostructured materials.

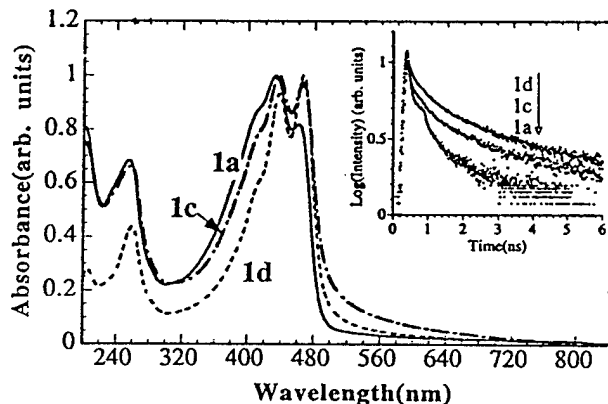


Figure 2. Optical absorption spectra of thin films of 1a, 1c, 1d and inset shows PL decay dynamics for emission at 550nm ($\lambda_{ex} = 380\text{nm}$).

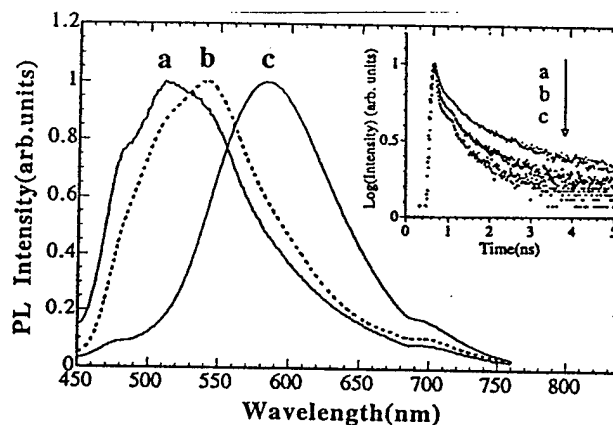


Figure 3. PL emission ($\lambda_{ex} = 420\text{nm}$) spectra of 1c thin films prepared by different processes. Inset shows PL decay dynamics of 1c thin films for emission at 510, 540, 560nm for a,b,c respectively ($\lambda_{ex} = 380\text{nm}$).